

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C23C 22/68, C09D 5/08, 143/02	A1	(11) International Publication Number: WO 00/55391 (43) International Publication Date: 21 September 2000 (21.09.00)
(21) International Application Number: PCT/GB00/00611 (22) International Filing Date: 22 February 2000 (22.02.00) (30) Priority Data: 9905600.4 12 March 1999 (12.03.99) GB (71) Applicant (for all designated States except US): ALBRIGHT & WILSON UK LIMITED [GB/GB]; 210-222 Hagley Road West, Warley, West Midlands B68 0NN (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ARCHER, Adrian, Charles [GB/GB]; 112 Jeffcock Road, Pennfields, Wolverhampton, West Midlands WV3 7AF (GB). RUSH, Susan, Marie [GB/GB]; 10 Hawkswell Drive, Hadley Heath, Willenhall, West Midlands WV13 3EJ (GB). (74) Agent: BARKER BRETTELL; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: TREATING METAL SURFACES (57) Abstract A metal treatment composition comprises silica, one or more organo-phosphonates (or organo-phosphonate species) and/or one or more organo-phosphates (or organo-phosphate species), together with a carrier. The composition can be applied to the surface of a metal to enhance the resistance of the metal to corrosion and/or to enhance the adhesion to the treated metal of further coatings.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LJ	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TREATING METAL SURFACES

The present invention relates to a composition for treating metal surfaces, to a process for treating metal surfaces with the composition and to metal
5 surfaces treated by means of such a process.

Metal surfaces are prone to corrosion, which weakens the strength of the metal over a period of time. There are many products available which help prevent the corrosion of metals. In many cases, however, the
10 product is specific for one metal and therefore must be changed with the metal, which can lead to waste and cross-contamination.

Many known coating compositions contain chromium compounds. However, there is increasing pressure to remove chromium compounds
15 from metal pretreatments and there are a number of known chromium-free processes. These known processes tend to be complicated and to require the use of catalysts and accelerators to speed up the coating process. The catalysts and accelerators may also need to be varied according to the metal surface.

20

Subsequent to treatment with a corrosion inhibitor, the metal surface often has one or more further coatings (e.g. paint) applied thereto and accordingly the coating composition should permit or promote good adhesion of such further coatings.

25

Our published European Patent Specification EP-B-0273698 discloses a composition for treating metal surfaces, in which the composition comprises a dispersion of silica in an aqueous solution of an acidic iron or aluminium compound.

30

Our co-pending application No. GB 9826851.9 discloses another composition for treating metal surfaces, in which the composition includes one or more organo-phosphonates or organo-phosphonate species.

5 We have now found that a metal treatment composition which includes both silica and one or more organo-phosphonates or organo-phosphonate species can be used to treat metal surfaces of all kinds to enhance the resistance of the metal to corrosion and/or to enhance the adhesion to the treated metal of further coatings.

10

We have further found that the composition according to the present invention can include one or more organo-phosphates or organo-phosphate species.

15 Accordingly, the present invention provides a composition suitable for use in the treatment of metal surfaces, the composition comprising silica, one or more organo-phosphonates or organo-phosphonate species and/or one or more organo-phosphates or organo-phosphate species, together with a carrier for the composition.

20

Preferably, the silica is of small particle-size.

Amorphous silica, which has been obtained pyrogenically from silicon tetrachloride, or which has been precipitated in an aqueous medium from
25 alkali silicates, may be used. Thus, the silica is usually hydrophilic, non-crystalline and colloidal. The silica particles usually have an average particle size of less than 170 nm, but may have a particle size in the range 1-200 nm, preferably 1-50 nm, for example 4-30 nm and especially 8-20 nm.

30

The organo-phosphonate or organo-phosphonate species included in the composition of the present invention may be a mono-or di-phosphonic acid, ester or salt, especially with one or more unsaturated carbon-to-carbon bonds.

5

The phosphonic acid may thus be an alkyl, aryl or alkenyl phosphonic acid such as octyl phosphonic acid, phosphonosuccinic acid, phosphonopropanoic acid, vinylphosphonic acid (VPA), vinylidene-1, 1-diphosphonic acid (VDPA) or phenyl VPA.

10

The organo-phosphonate or organo-phosphonate species may comprise a polymer with pendant phosphonic or di-phosphonic acid groups.

Thus, the composition may include a homopolymer of a phosphonic acid
15 such as vinylphosphonic acid (VPA), vinylidene-1, 1-diphosphonic acid (VDPA), phenyl VPA, or a salt or an ester of any of the said acids.

Alternatively, the composition may include a copolymer of a phosphonic acid (or a salt or an ester of said acid) together with a second co-
20 monomer.

The second co-monomer may be an unsaturated carboxylic acid, such as acrylic acid, maleic acid or methacrylic acid (or salts or esters of any of the said acids).

25

The second co-monomer may alternatively be an unsaturated sulphonic acid, such as vinylsulphonic acid (VSA), or acrylamido methyl propane sulphonic acid (AMPS), (or an ester or a salt of any of the said acids).

The second co-monomer may be any other unsaturated compound (such as
30 acrylonitrile) which is co-polymerisable with the phosphonic acid.

Again, the composition may include a terpolymer of an unsaturated phosphonate species and other suitable comonomers such as an unsaturated sulphonic acid, an unsaturated carboxylic acid or acrylamide.

- 5 For example, the composition may include a terpolymer of VPA, VSA and acrylic acid.

Alternatively the composition may include a polyester containing pendant phosphonic acid groups.

10

The organo-phosphate or organo-phosphate species included in the composition of the present invention may be an alkylene acrylate phosphate monomer, oligomer or homopolymer. Suitable alkylene acrylate phosphates include ethylene methacrylate phosphate.

15

Alternatively, the alkylene acrylate phosphates can be present in the composition of the present invention as copolymers, for example copolymers with unsaturated acids such as acrylic acid, methacrylic acid and salts and esters of these acids.

20

The ratio of silica to the organo-phosphonate and/or organo-phosphate in the compositions of the present invention must be such as to ensure a coherent coating with adequate covering properties.

- 25 The most convenient material for use as a carrier for the composition is water.

The present invention also provides a process for treating metal surfaces with compositions as hereinabove described, in which the process includes
30 the steps of (a) making a composition according to the present invention,

(b) applying the composition to a metal surface and (c) causing or permitting the so-applied composition to dry to form an adherent coating on the metal surface.

- 5 Step (a) of the process may conveniently be carried out by dispersing the silica in water by means of a high-speed disperser and mixing into the dispersion the organo-phosphonate or organo-phosphate component.

- Step (b) may be carried out by painting, dipping, spraying or roller-coating the composition on to the metal surface to be treated.
- 10

- In accordance with one embodiment of the process of the present invention, the amount of composition to be applied to the metal surface may be controlled by dilution of the composition and adjustment of the wet film thickness.
- 15

Preferably the amount of composition residue left on the surface after drying is in the range of 0.001g/m^2 to 10.000g/m^2 , more preferably 0.005g/m^2 to 5.000g/m^2 and most preferably $0.01\text{-}1.00\text{g/m}^2$.

20

- The composition may be applied to the metal surface by flood-spraying or immersion, the wet film being preferably metered to the required thickness (for example by means of one or more sets of squeegee rollers). The excess composition may be recovered and reused. Alternatively, the composition may be applied by roller-coating onto the metal surface. Roller-coating gives a more uniform coating than flood-spraying followed by squeegeeing and avoids waste of the composition.
- 25

In accordance with a second embodiment of the process of the present invention, the amount of composition to be applied to the metal surface may be controlled by a reaction occurring between the metal surface and the composition.

5

Preferably the surface is immersed in the composition, or an aqueous solution thereof, suitably for between 0.5 seconds and five minutes at a temperature of between 5°C and 100°C.

- 10 The metal surface may be wiped or rinsed after contact with the composition to remove any unbound composition.

The composition is preferably applied as an aqueous solution.

- 15 Step (c) may be carried out by allowing the composition to dry passively at ambient temperature. Alternatively, the composition may be dried positively at a temperature of 60-200°C for 0.1-10 minutes, preferably at 80-180°C for 0.1-5 minutes, for example at 140-180°C for 0.5-2 minutes.

- 20 The process according to the present invention is applicable to any metal surface.

The metal surface to which the composition is to be applied may be pre-cleaned, for example by treatment with an aqueous acid or alkaline

- 25 degreasing preparation and brushing.

The metal surface to which the composition has been applied may be wiped or rinsed.

7

The advantages of these methods of application of the composition include the uniform application of the composition to the metal surface, the low capital cost and the possibility of recycling excess composition to avoid waste.

5

The present invention further provides a metal surface treated by the process described hereinabove.

CLAIMS

1. A composition suitable for use in the treatment of metal surfaces,
the composition comprising silica, one or more organo-
5 phosphonates or organo-phosphonate species and/or one or more
organo-phosphates or organo-phosphate species, together with a
carrier for the composition.
2. A composition according to Claim 1, in which the silica has an
10 average particle size of less than 170nm.
3. A composition according to Claim 2, in which the silica has an
average particle size of 1-200nm.
- 15 4. A composition according to Claim 2 or 3, in which the silica has an
average particle size of 1-50nm.
5. A composition according to Claim 2, 3 or 4, in which the silica has
an average particle size of 4-30nm.
20
6. A composition according to any one of Claims 2 to 5, in which the
silica has an average particle size of 8-20nm.
7. A composition according to any one of Claims 1 to 6, in which the
25 organo-phosphonate or organo-phosphonate species is a mono - or
di-phosphonic acid, ester or salt.
8. A composition according to Claim 7, in which the organo-
phosphonate or organo-phosphonate species is an alkyl, aryl or
30 alkenyl phosphonic acid.

9. A composition according to Claim 8, in which the phosphonic acid is octyl phosphonic acid, phosphono-succinic acid, phosphono-propanoic acid, vinylphosphonic acid (VPA), vinylidene-1,1-diphosphonic acid (VDPA) or phenyl VPA.
- 5
10. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or organo-phosphonate species comprises a polymer with pendant phosphonic or di-phosphonic acid groups.
- 10 11. A composition according to Claim 10, in which the organo-phosphonate or organo-phosphonate species comprises a homopolymer of VPA, VDPA, phenyl VPA or a salt or an ester of any of said acids.
- 15 12. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or organo-phosphonate species comprises a copolymer of a phosphonic acid (or a salt or an ester of said acid) together with a second comonomer.
- 20 13. A composition according to Claim 12, in which the second comonomer is an unsaturated carboxylic acid.
14. A composition according to Claim 12 or 13, in which the second comonomer is acrylic acid, maleic acid or methacrylic acid (or a
- 25 salt or an ester of any of said acids).
15. A composition according to Claim 12, in which the second comonomer is an unsaturated sulphonic acid.

16. A composition according to Claim 15, in which the second comonomer is vinyl sulphonic acid (VSA), acrylamido methyl propane sulphonic acid (AMPS) or an ester or a salt of either of said acids.
- 5
17. A composition according to Claim 12, in which the second comonomer is acrylonitrile.
- 10
18. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or orgno-phosphonate species comprises a terpolymer of an unsaturated phosphonate and two comonomers selected from the group consisting of unsaturated sulphonic acids, unsaturated carboxylic acids and acrylamide.
- 15
19. A composition according to Claim 18, in which the terpolymer is a terpolymer of VPA, VSA and acrylic acid.
- 20
20. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or organo-phosphonate species comprises a polyester containing pendant phosphonic acid groups.
- 25
21. A composition according to any one of the preceding claims, in which the organo-phosphate or organo-phosphate species is an alkylene acrylate phosphate monomer, oligomer or homopolymer.
22. A composition according to Claim 21, in which the alkylene acrylate phosphate is ethylene methacrylate phosphate.
- 30
23. A composition according to any one of Claims 1 to 20, in which the organo-phosphate or organo-phosphate species is a copolymer

of an alkylene acrylate phosphate with an unsaturated acid (or a salt or ester of such an acid).

24. A composition according to Claim 23, in which the unsaturated
5 acid is acrylic acid or methacrylic acid.

25. A composition according to any one of the preceding claims, in which the carrier is water.

10 26. A process for treating metal surfaces with a composition according to any one of Claims 1 to 25, said process comprising the following steps:

15 (a) making said composition by dispersing the silica in water and mixing into the dispersion the organo-phosphonate or organo-phosphate component;

(b) applying said composition to a metal surface;

20 (c) causing or permitting the so-applied composition to dry to form an adherent coating on said metal surface.

27. A process according to Claim 26, in which step (b) is carried out by painting, dipping, spraying, or roller-coating the
25 composition on to the metal surface.

28. A process according to Claim 26 or 27, in which the amount of composition residue left on the metal surface after drying is in the range 0.001 g/m² to 10.000 g/m².

29. A process according to Claim 28, in which the amount of composition residue left on the metal surface after drying is in the range 0.001 g/m² to 5.000 g/m².
- 5 30. A process according to Claim 28 or 29, in which the amount of composition left on the metal surface is in the range 0.01 g/m² to 1.00 g/m²..
- 10 31. A process according to any one of Claims 26 to 30, in which the metal surface is immersed in the composition or an aqueous solution of said composition for between 0.5 seconds and 5 minutes at a temperature of between 5°C and 100°C.
- 15 32. A process according to any one of Claims 26 to 31, in which step (c) is carried out by allowing the composition to dry passively at ambient temperature.
- 20 33. A process according to any one of Claims 26 to 31, in which step (c) is carried out by drying the composition at 60°C to 200°C for 0.1 to 10 minutes.
34. A process according to Claim 33, in which the composition is dried at 80°C to 180°C for 0.1 to 5 minutes.
- 25 35. A process according to Claim 33 or 34, in which the composition is dried at 140°C to 180°C for 0.5 to 2 minutes.
36. A process according to any one of Claims 26 to 35, in which the metal surface is pre-cleaned before step (b).

37. A process according to Claim 36, in which the pre-cleaning of the metal surface is carried out by means of treatment with an aqueous acid or alkaline de-greasing preparation, followed by brushing.
- 5 38. A process according to any one of Claims 26 to 37, in which, after stage (c), the coated surface is wiped or rinsed.
39. A process according to Claim 26, substantially as hereinbefore described.
- 10 40. A metal surface which has been treated by a process according to any one of Claims 26 to 39.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C23C22/68 C09D5/08 C09D143/02		Inter. Appl. No. PCT/GB 00/00611
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C23C C09D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 351 675 A (GUHDE DONALD J) 28 September 1982 (1982-09-28) column 5, line 66 -column 8, line 40	1-7, 25-27, 31-35, 37, 40
X	WO 95 04169 A (HENKEL CORP) 9 February 1995 (1995-02-09) example 17B	1-7, 25-30, 32-37, 40
X	US 4 170 671 A (HIRASAWA YOUJI ET AL) 9 October 1979 (1979-10-09) claims 1,11; example 5	1-6, 21-24, 26
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">6 June 2000</div>	Date of mailing of the international search report <div style="text-align: center;">14/06/2000</div>	
Name and mailing address of the ISA European Patent Office, P.O. 8015 Paternoster 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 apo nl, Fax: (+31-70) 340-3016	Authorized officer <div style="text-align: center;">Torfs, F</div>	

INTERNATIONAL SEARCH REPORT

Inter- national Application No
PCT/GB 00/00611

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 341 558 A (YASHIRO KUNIIJI ET AL) 27 July 1982 (1982-07-27) claims 1,5,6; example 1	1-6, 25-30, 33-36,40
X	WO 95 09934 A (HENKEL CORP) 13 April 1995 (1995-04-13) example 6	1-6, 25-30,40
X	EP 0 583 769 A (KAWASAKI STEEL CO) 23 February 1994 (1994-02-23) page 4, line 22-57; claims 1-4	1-6, 26-30
A	US 3 293 088 A (HERBST W.) 20 December 1966 (1966-12-20) claims 1-4	7,8, 10-14,17
P,A	GB 2 331 942 A (ALBRIGHT & WILSON UK LTD) 9 June 1999 (1999-06-09) cited in the application claims 1-19	7-16,20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00611

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4351675 A	28-09-1982	NONE	
WO 9504169 A	09-02-1995	US 5427632 A AT 163978 T BR 9407110 A CN 1128053 A,B DE 69408996 D DE 69408996 T EP 0713540 A HK 1007660 A JP 7145486 A SG 52743 A US 5449415 A ZA 9405474 A	27-06-1995 15-03-1998 27-08-1996 31-07-1996 16-04-1998 08-10-1998 29-05-1996 16-04-1999 06-06-1995 28-09-1998 12-09-1995 03-03-1995
US 4170671 A	09-10-1979	NONE	
US 4341558 A	27-07-1982	NONE	
WO 9509934 A	13-04-1995	US 5356490 A AU 676950 B AU 7956794 A BR 9407751 A CA 2172632 A CN 1132531 A DE 69422420 D EP 0728225 A US 5534082 A US 5769967 A ZA 9407354 A	18-10-1994 27-03-1997 01-05-1995 12-02-1997 13-04-1995 02-10-1996 03-02-2000 28-08-1996 09-07-1996 23-06-1998 10-05-1995
EP 0583769 A	23-02-1994	CA 2104058 A JP 2793945 B JP 6234187 A KR 9602636 B US 5514483 A	18-02-1994 03-09-1998 23-08-1994 24-02-1996 07-05-1996
US 3293088 A	20-12-1966	CH 419401 A DE 1184588 B DE 1188411 B FR 1280107 A GB 935955 A NL 128296 C NL 257772 A	04-05-1962
GB 2331942 A	09-06-1999	NONE	